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*THE ADHESION BETWEEN MERCURY, WATER, AND  
ORGANIC SUBSTANCES, AND THE FUNDAMENTAL  
PRINCIPLES OF FLOTATION*

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Communicated by W. A. Noyes, October 14, 1919

The primary purpose of this investigation was to determine the effects of the molecular attraction at the surface of a metal, and to compare these effects with those of the surface of an oxygen compound such as water. Since the flotation process depends upon the preferential wetting and adhesion of gas films on metals, including the heavy sulphides, etc., on the one hand and silica and similar substances on the other, the general principles learned in connection with such a study, should be fundamental for the study of the process. I have been informed by Dr. E. C. Bingham that the adhesion between organic substances and metals is also fundamental with respect to the characteristics of lubricants.

The equation of Dupré<sup>1</sup> and that of Harkins, both of which are based on pure thermodynamics, give us the most accurate means for the study of the effects of molecular attraction at surfaces. The equation of Dupré gives the *adhesional work* done during the approach of 1 sq. cm. of one surface to meet the same area of the other. This is numerically equal to the work necessary to pull the two surfaces apart. The work of approach is also equal to the decrease of free surface energy ( $-\Delta\gamma$ ) during the process which is given by the equation

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

where  $\gamma_1$  and  $\gamma_2$  give the free energy of the two unlike surfaces before their approach, and  $\gamma_{1,2}$  is the free energy of the interface.

The equation of Harkins gives the *total energy of approach* ( $E_A$ ) and this may be called the *total adhesional energy*, as follows:

$$E_A = -\Delta E_S = (\gamma_1 + l_1) + (\gamma_2 + l_2) - (\gamma_{1,2} + l_{1,2})$$

where  $l$  represents the latent heat of the surface or interface in ergs per square centimeter. The total adhesional energy is closely related to the molecular surface attraction, while the adhesional work is the tensile force necessary to pull the two surfaces apart, integrated through the distance which they move during separation, but given a negative sign.

The data obtained in this laboratory indicate that the adhesional work between a mercury surface and the surface of an organic liquid is always greater, at least for all substances investigated, than that between the same organic liquid and water, and also greater than that between the organic liquid and itself. This last might be more properly described by the term *cohesive surface work*. A second point of interest is that for about half the organic substances investigated, the *difference* between the adhesional work against mercury and that against water, is nearly constant, with a value between 80 and 92 ergs. This is true for such liquids as the paraffin hydrocarbons, benzene, toluene, the xylenes, carbon tetrachloride, chloroform, and nitrobenzene, so *the work is by no means entirely specific*. On the other hand the adhesional work toward water is specifically high in the case of the alcohols, water and ether, while that toward mercury is very high in the case of the compounds of sulphur, iodine, and bromine, and also oleic acid, which indicates that the specific effects are very marked.

At the interface between organic compounds and water, groups which contain oxygen or nitrogen, double or triple bonds, orient toward the water; at a mercury surface the sulphur, bromine, or iodine, should turn toward the mercury.

In order to illustrate these relations a few of the data obtained in the laboratory are presented in table 1. The experimental work on mercury was done under my direction by Dr. E. H. Grafton and Warren W. Ewing, while that on water was selected from an extensive set of data obtained by Drs. F. E. Brown, G. L. Clark, E. C. H. Davies, Mr. L. E. Roberts, and Mr. Y. C. Cheng.

The well known rule of Antonow<sup>2</sup> states that the interfacial tension between two liquids is equal to the surface tension of the liquid which has the higher surface tension minus that which has the lower surface tension. Where this rule does not hold for an interface organic liquid-water, the discrepancy is explained by Antonow as due to the fact that the interface is between two solutions and not two pure liquids, so the surface tensions used should be those of the solutions or phases, instead of the pure liquids. The Antonow rule sprang from the idea that an interface at the two individual surfaces still exists, but that one acts in a negative sense on the other. This rule is in direct discordance with the theory developed independently by Langmuir and by Harkins, that the molecules in surfaces and interfaces are oriented. This theory need not be discussed here, since the above table clearly proves the Antonow rule to be incorrect for immiscible liquids. Thus his rule if it were applica-

TABLE 1

THE ADHESIONAL WORK BETWEEN MERCURY, WATER, AND ORGANIC LIQUIDS, WITH THE COHESIONAL SURFACE WORK IN ORGANIC SUBSTANCES FOR COMPARISON. (LIQUIDS ARRANGED IN ORDER OF ADHESIONAL WORK TOWARD MERCURY)  
(IN ERGS PER SQUARE CENTIMETER)

(1) LIQUID	(2) INTERFA- CIAL TEN- SION* AGAINST MERCURY	(3) ADHE- SIONAL WORK AGAINST MERCURY	(4) COHE- SIONAL WORK AGAINST ITSELF	(5) DIFFER- ENCE (3) MINUS (4)	(6) ADHE- SIONAL WORK AGAINST WATER	(7) DIFFER- ENCE MERCURY MINUS WATER (3-6)
(Air).....	465					
Hexane.....	378	120	36.9	83	40	80
Ethyl ether.....	379	123	43.6	79	73	50
Octane.....	375	127	43.5	83	44	83
Carbon tetrachloride.....	362	150	53.3	97	56	94
Chloroform.....	357	155	54.3	101	67	88
Benzene.....	363	146	57.6	88	67	79
Toluene.....	359	151	58.0	93	67	84
m-Xylene.....	357	152	58.0	94	64	88
o-Xylene.....	359	153	58.0	95	67	86
p-Xylene.....	361	155	54.0	101	64	91
Iso-butyl alcohol.....	348	155	45.6	109	94	61
Secondary octyl alcohol.....	348	159				
Octyl alcohol.....	352	161	55.1	106	92	69
Methylene chloride.....	341	169	53.0	116	71	98
Ethylidene chloride.....	337	174	49.2	125		
Nitrobenzene.....	350	173	86.8	86	91	82
Carbon bisulfide.....	336	175	62.8	113	56	119
Aniline.....	341	181	85.2	96	110	71
Water.....	375	182	145.6	36	145.6	36
Oleic acid.....	322	191	65.0	136	89.6	101
Ethyl iodide.....	322	195	56.4	139	63	132
Ethylene bromide.....	326	197	77.4	120	75	122
Methyl iodide.....	304	211				
Acetylene tetrabromide.....	293	230	99.3	131	84	146
Mercury.....		960	960.0		182.6	(778)

ble to the pure liquids would state that the interfacial tension between mercury and acetylene tetrabromide is 430, while the experimental value is 293, an extremely great deviation. Taking another example at random it is found that the Antonow rule in this form gives the mercury-octyl alcohol interfacial tension as 452, while the experi-

mental value is 352. As a matter of fact, the deviation between the result given by rule and by experiment seldom falls below 90 ergs, and is often higher, which seems to disprove the rule.

In spite of the above objections it must be admitted that Antonow's rule has been of considerable use in connection with phase boundaries between water and organic liquids. It should be realized, too, that the above objections to it involve a certain hypothesis, that is that the amount of the organic liquid dissolved in the mercury is too small to reduce the surface tension by 90 ergs or more when the mercury phase is split apart in such a way as to form surfaces from the interior part of the mercury phase.

Preliminary experiments on the adsorption of benzene and other vapors on a mercury surface show that their positive adsorption is very much greater than on a water surface at the same concentration of vapor. Water present either in the air or in such organic liquids as hexane, benzene, ether, etc., is also adsorbed positively, and the adsorption is very marked even when only a very small amount of water is present. Mercury salts, such as mercurous iodide or bromide, when dissolved in an organic iodide or bromide, are strongly adsorbed. The high adsorption of such substances on mercury as compared with that on water is in accord with my theory that the adsorption increases in general with the rate of drop in the intensity of the electromagnetic intermolecular stray field at the surface of the liquid, since this drop is very much more rapid for mercury than for water. According to the results obtained by F. Schmidt<sup>3</sup> caesium, rubidium, and potassium, when dissolved in mercury are strongly, and sodium, tin, lead, and gold, are slightly positively adsorbed. Negative adsorption is most marked with barium as a solute, and to a lesser extent with strontium, calcium, cadmium, zinc, thallium, and lithium, in decreasing order of effect.

The experimental difficulties in connection with the investigation of the surface of a liquid metal are considerable, and they have been solved thus far by Dr. Grafton and Mr. W. W. Ewing. The result which is used in table 1 for the surface tension of mercury in a vacuum, is not our own, and may be too high, but this would not affect the value of the results, since it introduces only a small constant difference in all of the numbers which represent the work of adsorption. The liquids were purified with great care. Many supposedly pure organic substances which are not sulphur compounds, and which have the correct boiling points, contain enough organic sulphides to make determinations made upon them entirely useless. This was especially true of the xylenes, which were boiled with mercury for several days to remove the sulphur.

Experiments have been made on the adsorption of organic acids from aqueous solution, and the results finally obtained, together with those on soaps, all of which have a high positive adsorption, will be reported in the complete papers which will be published in the *Journal of the American Chemical Society*. A recent paper by Hardy<sup>4</sup> gives valuable information on the application of the principles of surface action to the problem of lubrication. Hardy was the first worker to investigate the application of the Dupré equation to interfaces between water and organic liquids. Our complete papers will consider the relation between adhesion and lubrication. Experiments are now in progress on the heat of adsorption of liquids on solids, both on dispersiod and plane surfaces, and calculations are in progress which will relate the results given in this paper to the atomic and molecular distances.

<sup>1</sup> Dupre, *Theorie Mécanique de la Chaleur*, Paris, 1869, p. 69; Lord Rayleigh, Phil. Mag. (5) **30**, (1890), (461), Hardy, *Proc. Roy. Soc., London*, (A) **88**, 1913, (303-33), Harkins, Brown, and Davies, *J. Amer. Chem. Soc.*, **39**, 1917, (354-64).

<sup>2</sup> Antonow, *J. Chem. Phys.*, **5**, 1907, (384).

<sup>3</sup> F. Schmidt, *Leipzig, Ann. Physik*, **39**, 1912, (1108).

<sup>4</sup> Hardy, *Phil. Mag.*, May, 1919.

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## A BENIGN TUMOR THAT IS HEREDITARY IN DROSOPHILA

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*1. A non-lethal hereditary tumor.*—In a strain of flies with a lethal tumor, i.e. a tumor occurring in one-half of the males and causing their death (*J. Canc. Res.*, July, 1918; *J. Exper. Zool.*, February, 1919) another tumor has appeared as a mutation. The new tumor differs from the lethal one in that it is not sex-linked, i.e., it appears in females as well as males, and further in that it does not cause the death of the flies in which it occurs.

After several generations of inbreeding of males and females with tumors, a stock was obtained which breeds true to the tumor—the tumor appearing in all the flies.

Since the new tumor is not sex-linked its gene is not located in the X chromosome. To locate the gene in one of the other chromosomes, females with tumors were mated to star dichaete males. The gene for